



Applicant : Verhaak, Michael Johannes Franciscus Maria
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For : REDUCTION OF N_2O EMISSIONS
Examiner: : Mr. J. Strickland

Declaration under 37 CFR 1.132

1. I, Rudolf Willem van den Brink, Ph.D., do hereby declare and say as follows:
2. I have a Ph.D. degree in Chemistry from the Leiden University, in Leiden, The Netherlands and I Graduated in 1999. The subject of my thesis was catalytic combustion of chlorinated hydrocarbons. I received my masters (doctorandus) degree in chemistry from the University of Amsterdam, Amsterdam the Netherlands in 1994.
3. Since 1999 I have been working in the Energy Research Centre of the Netherlands (STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND), in Petten, the Netherlands. From then I worked on the catalytic abatement of nitrous oxide from the nitric acid industry, from 2000 as a project leader. I co-ordinated several projects on the reduction of N_2O using hydrocarbons, both for government and corporate clients. Since 2003, I am manager of the Catalytic Emission Reduction Department of ECN.
4. My technical expertise is within the field of Environmental Catalysis and especially in the field of nitrous oxide, NO_x and VOC abatement. The iron-zeolite catalysts for N_2O reduction and decomposition has my special interest.
5. I am the principal author or co-author of more than 20 scientific papers in the technical field of Environmental Catalysis. I am the principal inventor or the co-inventor of three patent applications and patents.

UPON THE CATALYTIC REDUCTION OF N_2O EMISSIONS IN RELATION TO THE CATALYTIC REDUCTION OF NO EMISSIONS

6. I have been requested by STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND, the proprietor of the patent application to Verhaak, to provide comments on the catalytic reduction of N_2O in relation to NO and catalysts used for such catalytic reductions. I have read and understood the present patent application to Verhaak.
7. I have also read and understood the following documents: US 5149512, a publication of Li and Armor in Appl. Catal. B 3, 1993, a.o. page 56; Appl. Catal. 64, 1990, L1-L4 and Appl. Catal. B 25, 2000, 191-203.

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8. I was informed that the USPTO Examiner is of the opinion that US 5149512 would disclose the catalytic of N_2O with a saturated hydrocarbon. I respectfully disagree. My arguments can be divided in two points, first, what US5149512 teaches and second, what US5149512 enables:

a. TEACHING OF US 5149512

The background of US 5149512 teaches that NO_x refers to nitrogen dioxide NO_2 and nitric oxide NO (column 1, lines 16-18) and that the prior art does not disclose a catalytic process for destroying NO_x in oxygen rich combustion products (column 1, lines 31- column 3, line 36). The brief summary, detailed description and claims of US 5149512 teach that zeolites with Si/Al ratio greater than or equal to 2.5, which are exchanged with a cation and wherein the cation is selected from Co, Ni, Fe, Cr, Rh and Mn can be used for the conversion of NO_x with CH_4 (column 3, lines 45-55). It is further taught that the term NO_x comprises amongst others N_2O .

Further, the detailed description teaches two alternate embodiments.

In the first embodiment, the metal exchanged zeolite catalyst is subjected to a further metal exchange with cations, with metals represented by the third period transition metals and members of groups 8, 9 and 10 (US5149512: column 3, line 63 - column 4, line 2; column 7, lines 15-28; claim). It is unclear whether the metals for the further metal exchange have to be members of *both* the third period transition metals and of group 8, 9 and 10, but the examples of preferred cations in column 7, lines 23-24 *may suggest* that this is not the case. Hence, this embodiment may comprise zeolites which are exchanged with Co, Ni, Fe, Cr, Rh or Mn and which are *further exchanged* with Fe, Co, Ni, Ru, Pd, Ag, Hf, Th, W, Re, Os, Ir, Pt, Au or Hg. As (preferred) cations, only Co, Ni, Fe, Mn and Ag are *explicitly* mentioned in US 5149512 as second elements. No further elements belonging to this group of third period transition metals and group 8, 9 and 10 than Co, Ni, Fe, Mn and Ag are *explicitly* mentioned.

In the second alternate embodiment, the ion exchanged zeolite is impregnated with various anionic and neutral species. Suitable impregnating moieties include oxidizing metals selected from groups 5, 6, 7 and 11 (column 4, lines 7-8; column 7, lines 29-54; claim 7-9 (etc.)). Hence, this embodiment comprises zeolites which are exchanged with

Co, Ni, Fe, Cr, Rh or Mn and which are further impregnated with V, Cr, Mn, Cu, Nb, Mo, Tc, Ag, Ta, W, Re, Au. With respect to metals selected from groups 5, 6, 7 and 11 only Ag, and oxides of Nb, Mo, V and Mn are *explicitly* mentioned (column 7, lines 40-42; claim 9 (etc.)).

The examples of US 5149512 show that most of the examples are performed with ZSM-5 (17 out of 21). Further, 11 examples (runs 2, 4, 7a, 8, 9, 10, 11, 11a, 11b, 13, 14) are directed to ZSM-5 exchanged with one type of metals (of which 3 are reference examples (runs 2, 7a and 13), and from these eight single exchanged zeolites, *only* 2 are directed to Fe-exchanged zeolites (run 11b and 14). These Fe-exchanged zeolites are inferior to Co, Ni or Mn exchanged zeolites (table 2).

Further, from the examples, 9 examples (runs 3, 5, 6, 7, 17, 18, 19, 20, 21) are directed to ZSM-5 provided with 2 types of metals (of which 1 is a reference example (run 3)), and from these 8 examples of zeolites having two metal types, *none is directed to a zeolite with Fe*, but all 8 examples (100%) are directed to zeolites exchanged with cobalt.

Summarizing the teaching of US 5149512 and declaring the following:

1)

US 5149512 and the examples therein describe the conversion of NO (tables 1A, 2-9). This is stressed by the summary of the experiments in column 15, lines 24-33. I am of the opinion, based on my expertise, that catalysts which are suitable for conversion of NO and NO₂ are not necessarily suitable for conversion of N₂O (see also below)

2)

I derive from US 5149512 that zeolites exchanged with Fe can be used for the conversion of NO with methane (table 2). I do further derive that these Fe-exchanged zeolites are inferior to Co, Ni or Mn exchanged zeolites. I do however not derive from US 5149512 that a Fe exchanged zeolite for the conversion of N₂O with saturated hydrocarbons can be used.

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3)

I further learn from US 5149512 that for zeolites containing two ions, at least Co as catalytic ion is present. However, none of these Co-containing zeolites further comprise Ru, Rh, Pd or Au. The first and second alternate embodiments only describe explicitly the possibility of zeolites being exchanged with Co, Ni, Fe, Cr, Rh or Mn further being provided with (embodiment 1) Co, Ni, Fe, Mn and Ag or with (embodiment 2) Ag, and oxides of Nb, Mo, V and Mn. I derive from US 5149512 that the presence of Co is necessary in case zeolites are loaded with combinations of metals to obtain good results for NO reduction. I do not understand from US 5149512 that a Fe exchanged zeolite which is further provided with Ru, Rh, Pd or Au is suitable for the conversion of N_2O with saturated hydrocarbons.

b. ENABLEMENT OF US 5149512

The two embodiments from US 5149512

Referring to the two embodiments (for references to US 5149512, see above), the first alternate embodiment implicitly teaches 90 possible combinations of couples of metal ions. At least 4 of these possible combinations make no sense (Fe-Fe, Co-Co, Mn-Mn and Ni-Ni) to me. Further, some of the implicitly described possible combinations make no sense in chemical respect (e.g. ion exchanging with W or Hg?). I also do not understand that Mn is given as preferred cation, since it is neither a third period transition metal nor a group 8, 9 or 10 metal.

Referring to the second alternate embodiment, 72 combinations of 2 metals are implicitly disclosed. At least 2 of these implicitly disclosed possible combinations make no sense (Cr-Cr and Mn-Mn). Further, some of these implicitly described possible combinations make little sense in chemical respect (e.g. Tc?). Next to that, it is in my view unclear why these metals are anionic or neutral species. This embodiment becomes even more obscure since it stays undisclosed why Ag (explicitly disclosed; column 7 lines 24 and 40) Ta, W and Re are *anionic or neutral* species in alternate embodiment 2, *but cationic* species in alternate embodiment 1.

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Further, it is not taught how in this case these impregnations should be performed and how such metals must be impregnated as *anionic or neutral* (or perhaps both?) species.

Summarizing the disclosure of the two embodiments from US 5149512 and comments and declaring the following:

4)

US 5149512 does not clearly teach to me how the zeolites should be provided with a second metal: the groups with second metals are not clearly defined, combinations of metals which make no sense are suggested, metals serving both cationic and anionic properties seem to be suggested, inconsistency between description and examples are presented.

The reduction of N_2O with methane

None of the examples describe the conversion of N_2O (tables 1A, 2-9) but only show that NO can be converted. This is confirmed by the later publication of Li and Armor in Appl. Catal. B 3, 1993, on page 56) (see also above).

US 5149512 itself has different definitions for NO_x (on the one hand *including* N_2O : column 3, lines 56-58 and column 4, lines 44-47; and on the other hand *without* N_2O , column 1, lines 16-18, column 15, lines 24-30), thereby guiding to the interpretation of NO_x that is most likely to me: i.e. the interpretation of NO_x not being N_2O but being NO (and NO_2 , etc.), i.e. the interpretation as can further be derived from column 10, lines 6-8 in conjunction with column 10, lines 35 and 61, the interpretation of tables 1a, 2, 3, 4, 5, 6, 7, 8, and the interpretation of the header of table 9 and the remarks under table 9, each showing that NO_x is to be understood as NO but not as N_2O .

Further, it is known that the reduction of N_2O follows another mechanism than the reduction of NO and different catalysts are used. This is also conceivable, since the oxidation states of nitrogen in the compounds are different. Due to the different

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chemical behavior, the species are performing differently when brought into contact with a catalyst.

Proof of this can be found in Appl. Catal. 64, 1990, L1-L4, where it appears that reduction of NO_x with propane over a zeolite catalyst leads to the formation of N_2O (see also table 1 of this publication), which shows that this catalyst does not reduce NO_x and N_2O , but only NO_x ; this zeolite catalyst is therefore not suitable for the reduction of N_2O . Further proof can be found in Appl. Catal. B 25, 2000, 191-203, wherein it is shown that a first catalyst is used for the reduction of NO_x , whereby however large amounts of N_2O are formed. A second, zeolite based catalyst is necessary for the decomposition of N_2O . This shows that a zeolite based catalyst only cannot reduce efficiently both NO_x (NO) and N_2O .

In order to support that what is stated here as common knowledge has empirical basis, I have supervised the performance of additional experiments, which experiments are found in the appendix "Additional experiments", and which form part of this declaration, and which indeed show that catalysts that are suitable for reduction of N_2O are not necessarily suitable for the reduction of NO and vice versa.

The Fe-ZSM-5 and Pd/Fe-ZSM-5 catalysts used in the experiments were prepared according to the application to Verhaak.

The catalyst was entered into a glass plug flow reactor, which subsequently was installed in an oven. Gases were introduced via electronic Mass Flow Controllers and steam was introduced using a liquiflow meter followed by a controlled evaporator mixer. Gas compositions are given in the Appendix. Experiments were performed at atmospheric pressure. The reactor temperature was increased in steps and, after equalibration, gases leaving the reactor were analyzed using a FTIR gas analyzer. The conversions of N_2O and NO were calculated by comparing the concentrations at a given temperature with the concentrations of NO and N_2O measured when the reactor was bypassed (e.g. $(1 - [\text{N}_2\text{O}]_{\text{temp}} / [\text{N}_2\text{O}]_{\text{bypass}}) * 100\%$). The additional experiments are explained and presented in the appendix "Additional experiments".

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The experiments show that under exhaust gas conditions ZSM-5 exchanged with Fe (not according to the invention of Verhaak) provides good catalysts for the reduction of N_2O but performs badly for the reduction of NO with propane. The experiments further show that under exhaust gas conditions, ZSM-5-Fe,Pd (a catalyst according to Verhaak) is a good catalyst for the conversion with methane of N_2O , but a bad catalyst for the conversion with methane of NO. The experiments also show that under exhaust gas conditions yet a third catalyst, not according to Verhaak, provides a good catalyst for the reduction of N_2O but performs as catalyst badly for the reduction of NO (Appendices 1 - 3).

Hence, I hereby declare the following:

5)

With my knowledge, I derive from US 5149512 that the catalysts explicitly mentioned therein are only suitable for the reduction of NO, NO_2 , etc. (i.e. NO_x) and not necessarily for N_2O .

6)

From the additional data it appears that there is a general trend that catalysts suitable for N_2O reduction are not well applicable for NO reduction in SCR processes (and vice versa).

Summarizing the disclosure of N_2O reduction with methane from US 5149512 and declaring the following:

7)

US 5149512 does not provide a hint to me that a Fe exchanged zeolite, which is further provided with Ru, Rh, Pd or Au, is suitable for the conversion of N_2O with saturated hydrocarbons.

I hereby further declare the following:

8)

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The present invention claims the use of zeolites which contain two catalytically active metals, of which one is at least Fe and the second metal is one selected from the group consisting of Ru, Rh, Pd and Au, for the reduction with saturated hydrocarbons of N_2O .

9)

These zeolites are called promoted Fe-containing zeolites, since next to Fe, which may e.g. be applied to the zeolite by ion exchange, the zeolite further contains other active species selected from the group consisting of Ru, Rh, Pd and Au, which may e.g. be applied to the zeolite (containing Fe) by impregnation. The zeolite which is used in the process of the present invention is therefore a zeolite that can be described by:

Ru-Fe-Zeolite (e.g. Ru-Fe-ZSM-5)

Rh-Fe-Zeolite (e.g. Rh-Fe-ZSM-5)

Pd-Fe-Zeolite (e.g. Pd-Fe-ZSM-5)

Au-Fe-Zeolite (e.g. Au-Fe-ZSM-5)

10)

These zeolites are claimed for use in the method for the catalytic reduction of N_2O , which method provides a very suitable way to remove the environmental unfriendly N_2O from e.g. exhaust gasses. This method can e.g. be used next to the method of US 5149512, since these methods are complementary, the one removing N_2O , the other one removing NO_x (NO , NO_2 , etc.)

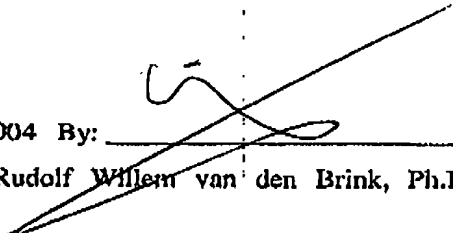
11)

The method of the invention provides additional benefits over prior art methods and may be of great value for basic chemicals production plants that emit N_2O , like those for the production of nitric acid or caprolactam, etc.

9. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that

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these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful statements may jeopardize the validity of the application or any patent issued thereon.

Date: 15-10-2004, 2004 By: 
Rudolf Willem van den Brink, Ph.D.

Appendices Additional Experiments

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Onze ref. P042963PCT/US AEL/ew

Appendix 1: Comparison of selective catalytic reduction of N₂O versus NO with methane using Fe-ZSM-5

Example N ₂ O-SCR with propane: performance Fe-ZSM-5	
Volume	10 ml
Flow	5 l/min
GHSV	30000 h ⁻¹
P	1 bara
Gascomposition	
N ₂ O	1500 ppm
NO	500 ppm
C ₃ H ₈	1500 ppm
H ₂ O	0.5 %
O ₂	2.5%
N ₂	bal.
N ₂ O conversion (%)	
T	Iron-ZSM-5
309	31
342	61
394	90
430	95
490	98
518	98

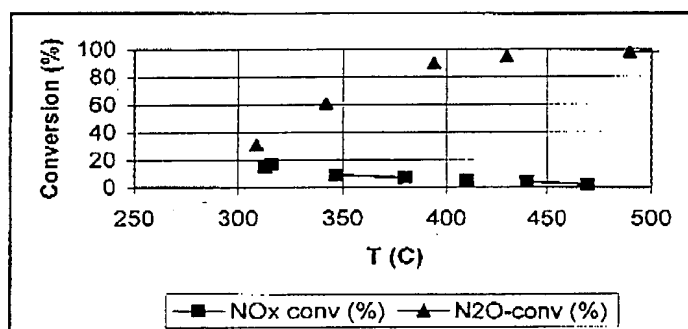
Example NO-SCR with propane: performance Fe-ZSM-5	
Volume	10 ml
Flow	5 l/min
GHSV	30000 h ⁻¹
P	1 bara

Gascomposition	
NO	500 ppm
C ₃ H ₈	1000 ppm
H ₂ O	0.5 %
O ₂	2.5%
N ₂	bal.

3

Onze ref. P042963PCT/US AEL/ew

	NO conversion (%)
T	Iron-ZSM-5
313	15
316	17
347	9
380	7
410	5
440	4
470	2

**CONCLUSION**

Iron performs at relevant temperatures much better in N₂O-SCR than in NO-SCR.

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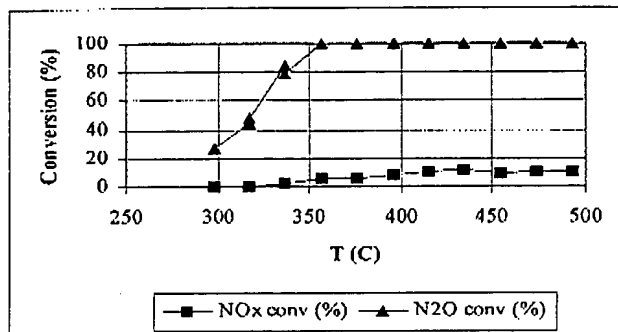
Onze ref. P042963PCT/US AEL/ew

Appendix 2: Comparison of selective catalytic reduction of N₂O versus NO with methane using Pd-Fe-ZSM-5

Example N ₂ O-SCR versus NO-SCR with methane: performance 0.15wt%PdFe-ZSM-5		
Volume	0.4 ml	
Flow	100 ml/min	
GHSV	15000 h ⁻¹	
P	1 bara	
Gascomposition	N ₂ O-SCR	NO-SCR
N ₂ O	1500 ppm	0 ppm
NO	0 ppm	500 ppm
CH ₄	1500 ppm	1500 ppm
H ₂ O	0.5 %	0.5 %
O ₂	2.5 %	2.5 %
N ₂	bal.	bal.
0.15%PdFe-ZSM-5		
T	N ₂ O conversion (%)	NO conversion (%)
298	26	0
337	85	2
356	100	6
375	100	6
414	100	10
433	100	11
471	100	10
490	100	10

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Onze ref. P042963PCT/US AEL/ew

**CONCLUSION**

0.15% PdFe-ZSM-5 performs, under conditions representative to exhaust gas, very good in N₂O-SCR. However, the same catalyst shows very poor activity in the NO-SCR.

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Onze ref. P042963PCT/US AEL/cw

Appendix 3: Comparison of selective catalytic reduction of N₂O versus NO with methane using a third catalyst

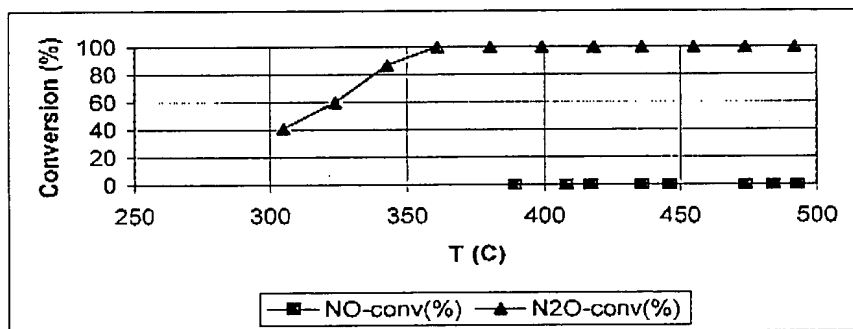
Example NO-SCR with methane: performance third catalyst		
Volume	0.4 ml	
Flow	100 ml/min	
GHSV	30000 h-1	
P	1 bara	
Gascomposition		
N ₂ O	0 ppm	
NO	500 ppm	
CH ₄	1500 ppm	
H ₂ O	10 %	
O ₂	5%	
N ₂	bal.	
third catalyst		
T	NO conversion (%)	methane conversion (%)
389	0	66
408	0	75
417	0	97
436	0	100
446	0	100
474	0	100
484	0	100
493	0	100

Example N ₂ O-SCR with methane: performance third catalyst	
Volume	0.4 ml
Flow	100 ml/min
GHSV	30000 h ⁻¹
P	1 bara
Gascomposition	

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Onze ref. P042963PCT/US AEL/ew

N ₂ O	500 ppm
NO	0 ppm
CH ₄	1500 ppm
H ₂ O	0.5 %
O ₂	2.5%
N ₂	bal.
third catalyst	
T	N ₂ O conversion (%) methane conversion (%)
305	41 21
324	60 37
343	87 77
361	100 100
380	100 100
399	100 100
418	100 100
436	100 100
455	100 100
474	100 100
492	100 100



Conclusion

The third catalyst performs under conditions representative to exhaust gas very good in N₂O-SCR, but very bad in NO-SCR.

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Simultaneous, catalytic removal of nitric oxide and nitrous oxide

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Abstract

The simultaneous, catalytic removal of nitrous oxide and nitric oxide in the presence of oxygen and methane or propane was studied over Co-ZSM-5. Methane is used for the reduction of nitric oxide while the nitrous oxide is able to compete for the metal sites to undergo simultaneous decomposition. Interestingly, while NO_x removal by methane does not readily occur without any oxygen, the presence of nitrous oxide actually enhances the conversion of nitric oxide in the absence of oxygen.

Key words: Co-ZSM-5, decomposition, nitrous oxide, nitric oxide, reduction, zeolites

INTRODUCTION

Nitrous oxide (N_2O) is now considered an environmental pollutant, because it contributes to catalytic stratospheric ozone destruction and is a greenhouse gas. Nitrous oxide continues to increase in the atmosphere, and this increase appears to be caused mainly by anthropogenic activities [1,2]. Man-made nitrous oxide may arise as a co-product from several processes, such as the use of circulating fluidized beds for combustion [3], automotive exhaust emissions [4], nitric acid production [5], and the production of large amounts of adipic acid for Nylon 66 [6]. With the increasing concerns about protecting our environment, there is a need to develop catalytic methods to avoid emission of nitrous oxide into the atmosphere. The impact of NO_x upon our environment is well established [7]. What is not widely appreciated is the fact that whenever one has nitric oxide emissions, nitrous oxide may also be produced [8]. Nitrous oxide may be produced during aerial oxidation below ca. 400°C , or whenever one oxidizes ammonia or organic amines at low temperatures ($<400^\circ\text{C}$) [9,10]. Today, the control of both nitrous oxide and NO_x emissions

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have become important. Few systems offer the ability to eliminate both these pollutants in one step.

Recently, we reported a catalytic process that efficiently reduces nitric oxide with methane in the presence of excess oxygen (reaction 1) [11,12]. We achieved 100% NO conversion at 400°C using various metal exchanged zeolites. Earlier we reported (reaction 2) [13,14] that one could use other metal exchanged zeolites for the



decomposition of nitrous oxide into its elements. Using selected metal zeolite catalysts, we now wish to report that one can remove both NO_x and nitrous oxide simultaneously.

EXPERIMENTAL

Na-ZSM-5 was prepared by a template free route and was first converted to NH_4^+ form by exchanging the zeolite with an NH_4NO_3 solution. Elemental analysis of this sample (Na, Al and Si) using inductively coupled plasma atomic spectroscopy indicated nearly complete Na^+ exchange by NH_4^+ ($\text{Na}/\text{Al} < 0.003$). Co-ZSM-5 was prepared by exchanging Co^{2+} into NH_4 -ZSM-5 suspended in an aqueous solution at 80°C. This exchange was carried out three times. After exchange the sample was washed, filtered and dried. The final product was then analyzed for Si, Al, and Co and has the following composition: 41.2% Si, 3.55% Al and 3.83% Co by weight ($\text{Si}/\text{Al}=11.0$, $\text{Co}/\text{Al}=0.49$). Thus, the ZSM-5 was 98% exchanged with Co^{2+} .

Catalytic activities were measured using a micro-catalytic reactor in a steady-state plug-flow mode. The reactor was a Quartz tube with 1/4 in. O.D. at the inlet and 3/8 in. at the outlet. A J-type thermocouple was in contact with the catalyst bed, and the temperature was controlled by a temperature programmer (Yokogawa Model UP40). The catalyst powder was pelletized, crushed and then sieved to 60-80 mesh before use. A 0.15 g Co-ZSM-5 sample was used for all reactions with a total gas flow of 100 cm^3/min , which resulted in a gas hourly space velocity (GHSV) of 20000 based on a zeolite with an apparent density of 0.5 g/cm^3 . The gas flows were independently controlled by a 4-channel mass flow meter/controller (Brooks 5850E), and the feed compositions, which differ for each reaction, are listed in the Tables 1-3. Certified standard gas mixtures, NO/He , CH_4/He , O_2/He , $\text{N}_2\text{O}/\text{He}$ and $\text{C}_3\text{H}_8/\text{He}$ (Air Products and Chemicals, Inc.) were used without further purification. The catalyst was pretreated with flowing helium at 500°C for 1 h before reaction. An on-line gas chromatograph (GC) (Varian 6000) with thermoconductivity detection (TCD) and a NO_x chemiluminescence analyzer (Thermo Environmental 42H) were

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used for the analysis. The GC with a Porapak Q column (8 ft. \times 1/8 in., 80/100 mesh at 30°C) was used to separate N_2O , CO_2 and CH_4 , and the NO_x analyzer for measuring NO_x (nitric oxide and nitrogen dioxide).

RESULTS AND DISCUSSION

The data presented in Table 1 illustrate the simultaneous removal of nitrous oxide and nitric oxide in the presence of methane and excess oxygen. This table also provides the conversions for the two control reactions: nitrous oxide decomposition (reaction 2) and nitric oxide reduction by methane (reaction 1). In the process of simultaneously removing nitric oxide and nitrous oxide, the nitric oxide and methane conversions are unchanged compared to those for nitric oxide reduction ($NO + CH_4 + O_2$) in the absence of nitrous oxide. The nitrous oxide conversions during simultaneous removal are reduced compared to those for nitrous oxide decomposition (for nitrous oxide in oxygen), and the degree of the decrease depends on the reaction temperature. At 400°C the nitrous oxide conversion changed from 56% for decomposition to 27% for the simultaneous removal. However, at 500°C, nearly complete nitrous oxide decomposition was obtained for both reactions. It appears that the sites for nitric oxide removal are not affected by the presence of nitrous oxide; however, the presence of nitric oxide reduced the number of sites for the nitrous oxide decomposition. Thus, at lower temperatures, the nitrous oxide conversion decreased. In contrast to nitric oxide reduction by methane, where nitric oxide conversion displays a volcano-shape curve with increasing temperature [11],

TABLE 1

Simultaneous removal of nitric oxide and nitrous oxide on Co-ZSM-5^a

T (°C)	N ₂ O decomposition ^b			MDN ^c			NO + N ₂ O removal ^d		
	400	450	500	400	450	500	400	450	500
N ₂ O conv. (%)	56	93	100	-	-	-	27	70	97 (82) ^f
NO conv. (%)	-	-	-	36	47	31	36	46	30 (24) ^f
CH ₄ conv. (%)	-	-	-	30	66	96	29	70	97 (77) ^f
C ₂ H ₆ conv. (%)	-	-	-	-	-	-	-	100	-

^a All reactions were run on a same catalyst, Co-ZSM-5, with a GHSV of 20 000 h⁻¹.

^b Feed: 788 ppm N₂O and 2.5% O₂ balance by He.

^c Feed: 850 ppm NO, 1200 ppm CH₄ and 2.5% O₂ balance by He; MDN means nitric oxide reduction by methane in the presence of O₂.

^d Feed: 788 ppm N₂O, 850 ppm NO, 1200 ppm CH₄ and 2.5% O₂ balance by He.

^e Feed: 788 ppm N₂O, 850 ppm NO, 600 ppm C₂H₆ and 2.5% O₂ balance by He; nitric oxide conversion = 69%, and nitrous oxide conversion = 68% at 450°C.

^f Same as in ^d but with the presence of 2% H₂O vapor in the feed.

nitrous oxide decomposition activity increases monotonically with temperature [18]. Consequently, the nitrous oxide conversion catches up with nitric oxide reduction by methane at higher temperatures. The notion that nitrous oxide decomposition and nitric oxide reduction may require different sites is supported by the fact that Mn-ZSM-5 and Ni-ZSM-5 are good catalysts for nitric oxide reduction by methane but poor catalysts for the nitrous oxide decomposition, and Cu-ZSM-5 is an effective catalyst for the nitrous oxide decomposition but inactive for the nitric oxide reduction. Co-ZSM-5, however, is active for both reactions. Here, we see parallel reactions occurring on the same catalyst. Independent experiments with Cu-ZSM-5 did not reveal substantial removal of nitric oxide in a mixture of NO, N₂O, CH₄, and O₂.

Water is known to be a reversible inhibitor [15] for NO_x removal by methane, and we observed some reduction in both NO_x and nitrous oxide conversion in the presence of 2% water vapor (Table 1). Also, it is well known that higher hydrocarbons will serve as reductants for NO_x in the presence of oxygen [16-18]. In one experiment we substituted propane (600 ppm) for methane (1200 ppm) and observed simultaneous removal of both nitric oxide and nitrous oxide (Table 1). These experimental conditions are similar to those of some industrial exhaust emissions, and the performance of this catalyst addresses several environmental concerns.

It is known that oxygen is essential for the effective reduction of nitric oxide by methane [11]. As illustrated in Table 2, in the absence of oxygen, the conversion of nitric oxide is less than 10% at 450°C; once oxygen is added, the nitric oxide conversion increases to 47%. However, when ca. 800 ppm of nitrous oxide is added to an NO + CH₄ stream that contains no oxygen, the nitric oxide conversion increases to 39%. Here, nitrous oxide serves as a source of oxygen. Recall (Table 1) that for the mixture of NO, N₂O, O₂ and CH₄, methane conversion remained unchanged with or without nitrous oxide. With nitrous oxide as an oxygen source, methane (as the nitric oxide reductant) is more efficiently utilized; the selectivity of methane is 66% vs. 25% with oxygen as an oxygen source. Nitrous oxide is known to be a selective oxidant for hydrocarbon oxidations [19-23]. It is known that nitrous oxide oxidizes methane

TABLE 2

Effect of oxygen and nitrous oxide on nitric oxide reduction by methane over Co-ZSM-5 at 450°C

Feed ^a	NO conversion (%)	N ₂ O conversion (%)	CH ₄ conversion (%)
NO + CH ₄ + O ₂	47	-	66
NO + CH ₄	7	-	3
NO + CH ₄ + N ₂ O	39	87	21

^a [NO] = 850 ppm, [CH₄] = 1200 ppm, [O₂] = 2.5%, and [N₂O] = 788 ppm. GHSV = 20 000 for all reactions.

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TABLE 3

Effect of methane on nitrous oxide decomposition over Co-ZSM-5 at 450°C

Feed ^a	N ₂ O conversion (%)	CH ₄ conversion (%)
N ₂ O only	93	-
N ₂ O + O ₂	92	-
N ₂ O + O ₂ + CH ₄	73	74
N ₂ O + CH ₄	99	42

^a [N₂O] = 1182 ppm, [CH₄] = 1200 ppm, [O₂] = 4.0%. GHSV = 20 000 for all reactions.

over Rh/Al₂O₃ [24]. Perhaps, the decomposition of nitrous oxide provides catalyst-bound atomic oxygen, which is more efficient in activating methane.

Table 3 describes the effect of the addition of oxygen and/or methane on nitrous oxide decomposition over Co-ZSM-5. The presence of oxygen appears to have no effect on the nitrous oxide decomposition activity on Co-ZSM-5, suggesting that its reaction rate is zero order in oxygen. However, when both oxygen and methane are added to the nitrous oxide stream, nitrous oxide conversion is decreased substantially, and there is also a significant degree of methane combustion. It seems that the methane combustion (CH₄ + O₂) competes with nitrous oxide decomposition for the same active sites. Interestingly, in the absence of oxygen, nitrous oxide conversion is enhanced by the presence of methane.

CONCLUSION

We report that selected metal on zeolite catalysts can simultaneously remove nitrous oxide and nitric oxide in the presence of methane or propane and excess oxygen. Specifically, Co-ZSM-5 is an active catalyst, and the presence of nitrous oxide actually enhances the reduction of nitric oxide by methane in the absence of any oxygen.

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L1

Highly selective reduction of nitrogen oxides with hydrocarbons over H-form zeolite catalysts in oxygen-rich atmospheres



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Keywords: nitrogen oxides reduction, zeolites, catalyst preparation (ion exchange).

INTRODUCTION

The emission of nitrogen oxides (NO_x : NO and NO_2) is now a global environmental problem. Two main catalytic technologies are currently available to decrease this emission. One is the three-way catalyst system for automobiles [1] and the other is the selective catalytic reduction process with ammonia for stationary sources [2]. Of the two processes, only the latter can be used to remove NO_x in oxygen-rich atmospheres. However, the use of ammonia makes this process unsuitable for small scale oxygen-rich NO_x emissions such as diesel engine exhausts.

Until now various systems of agents and catalysts have been tested to reduce NO_x , among which ammonia is the only reducing agent that can work under oxidizing conditions [3], although carbon monoxide [4,5] and hydrogen [6] were reported to be effective under certain limited conditions. Recently some attempts have been made to develop other effective systems. For example, Volkswagen A.G. [7] and Toyota Corporation [8] have patents of catalytic systems able to remove NO_x in auto exhausts with oxidizing atmospheres. They claim use of metal-containing zeolite catalysts and supported copper catalysts, respectively. However, the significance of the patents is not clear.

In an attempt to develop a catalytic method to selectively reduce NO_x without using ammonia, we have found that the reduction can occur to a high level even in the presence of a high concentration of oxygen when using H-form zeolite catalysts and small amounts of hydrocarbons as reducing agents. The present paper reports this new type of selective catalytic reduction of NO_x .

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L2

EXPERIMENTAL

As catalysts, H-ZSM-5, H-mordenite and HY were used along with Na-ZSM-5, silicalite, and silica gel as reference samples. H-ZSM-5 was prepared by ion-exchanging a parent ZSM-5 with ammonium nitrate solution, followed by calcination at 773 K. The parent ZSM-5 zeolite with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 62.7 was synthesized in an autoclave hydrothermally from sodium silicate, aluminium sulphate and tetrapropylammonium bromide as a template, followed by calcination at 793 K in air. H-mordenite was also prepared with the same ion-exchange method from commercial Na-mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 20.1$, Tosoh). HY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 49.7$) was a commercial zeolite (Tosoh). Na-ZSM-5 was synthesized by ion-exchanging the parent ZSM-5 with sodium nitrate solution. Silicalite was obtained from Union Carbide. Silica gel was super micro bead silica gel (Fuji-Davison).

The reactions were performed with a flow reactor by passing a mixed gas of 1079 ppm NO, 9.9% O_2 and 323 ppm hydrocarbon (propane or propene) in helium at a rate of $62 \text{ cm}^3 \text{ min}^{-1}$ (room temperature) over 1 g catalyst. The effluent gas was analyzed by gas chromatography. The catalytic activity was evaluated by the conversion of nitric oxide to nitrogen or nitrous oxide.

RESULTS AND DISCUSSION

Table 1 shows the percentage conversion of nitric oxide to nitrogen or nitrous oxide over various zeolite catalysts. The non-catalyzed reaction gave no nitrogen below 973 K. However, H-form zeolites had high activity for reduction of low concentrations of nitric oxide to nitrogen with small amounts of propane or propene even in the presence of about 10% oxygen. The effective temperature for the reduction of nitric oxide was between 473 K and 873 K. At lower temperatures, formation of nitrous oxide in small amounts was also observed. It should be noted that the selectivity of the hydrocarbon-nitric oxide reaction to the hydrocarbon-oxygen reaction is extremely high. This can be seen from the fact that the amount of hydrocarbon is only slightly in excess of the amount needed to reduce nitric oxide in the feed gas completely. Such high reaction selectivity has not been reported previously with the exception of reduction using ammonia.

Another point to be noted is the fact that the reduction occurs over catalysts containing no transition metal elements, for redox reactions are usually catalyzed by transition metals with variable oxidation states. With respect to the selective reduction with ammonia, however, H-form zeolite catalysts such as H-mordenite are reported to be effective [9].

The most active catalyst of the three H-form zeolites was H-mordenite, which gave the maximum nitric oxide conversion of 65% at 673 K, followed by H-ZSM-5 and HY. It is interesting that Na-ZSM-5 and silicalite were also active

L3

TABLE 1

Selective reduction of nitric oxide with hydrocarbons over zeolite catalysts

Catalyst	SiO ₂ /Al ₂ O ₃ mole ratio	Hydrocarbon	NO conv. to N ₂ / % (N ₂ O/%) at				
			473 K	573 K	673 K	773 K	873 K
H-ZSM-5	62.7	C ₂ H ₆		49 (6.5)	59 (0.8)	38 (0)	24 (0)
		C ₃ H ₈	38 (3.6)	50 (1.5)	24 (0.3)	9.8 (0)	5.8 (0)
H-mordenite	20.1	C ₃ H ₈		58 (8.9)	65 (1.3)	48 (0)	32 (0)
HY	49.7	C ₃ H ₈		9.0 (1.7)	19 (2.0)	26 (0.9)	22 (0)
		C ₄ H ₁₀	20 (2.2)	36 (1.0)	25 (1.7)	15 (0.4)	9.1 (0)
Na-ZSM-5	62.7	C ₃ H ₈	20 (6.3)	32 (2.8)	14 (1.7)	8.6 (0.5)	6.9 (0.2)
		C ₃ H ₆		14 (3.9)	22 (2.4)	19 (0.5)	12 (0)
silicalite		C ₃ H ₈					
silica gel		C ₃ H ₈		<0.4	<0.6	<1.1 (0.2)	<1.0 (0.3)

for the reduction although the activity was not so high. On the other hand silica gel showed no activity as can be seen from Table 1.

For all the catalysts, the percentage conversion of nitric oxide to nitrogen had a maximum at a certain reaction temperature. This optimum temperature varied with the type of zeolite catalysts. The use of propene instead of propane as the reducing agent lowered this temperature as can be seen from the data on H-ZSM-5 and HY. This suggests that the efficiency of the selective reduction depends not only on the reaction temperature but also on the type of zeolites and hydrocarbons.

To obtain further insight into the reaction, the selective reduction of nitric oxide with propene over H-ZSM-5 zeolite was examined in more detail. Fig. 1 indicates the variation of the percentage conversion of nitric oxide to nitrogen and the yield of carbon dioxide and carbon monoxide with temperature. At 873 K, propene was oxidized completely to carbon dioxide. At this temperature nitrogen was hardly formed. With decreasing reaction temperature, however, the yield of carbon dioxide decreased and carbon monoxide yield increased instead, whereas the conversion of nitric oxide to nitrogen reached a maximum at around 573 K. When nitric oxide was omitted from the reactant gas flow, the amount of carbon dioxide and carbon monoxide formed decreased slightly. It is suggested from these observations that the selective reduction is related to the catalytic activity of the zeolites for the oxidation of hydrocarbons.

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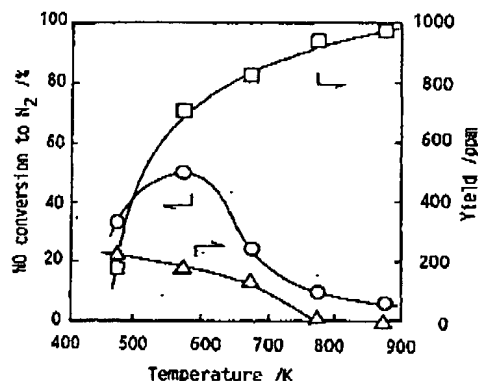


Fig. 1. Variation of the conversion of nitric oxide to nitrogen (O) and the yield of carbon dioxide (□) and carbon monoxide (Δ) with temperature in the selective reduction of nitric oxide with propene over H-ZSM-5. NO=1079 ppm, C₃H₆=323 ppm, O₂=9.9%.

We suspect that the active centres of the zeolites for selective reduction are their acid sites based on the fact that activity of H-ZSM-5 is higher than Na-ZSM-5 or silicalite and that silica gel is quite inactive. Further study is now in progress.

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Dual-bed catalytic system for NO_x – N_2O removal: a practical application for lean-burn deNO_x HC-SCR

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Abstract

A dual-bed catalytic system has been developed by which NO_x and N_2O are successively removed from flue gases, simulating lean-burn engine conditions. NO_x is removed in the first stage by selective catalytic reduction with propene over a Pt supported on activated carbon catalyst. The second bed decomposes the N_2O formed in the first bed into N_2 and O_2 . Catalysts tested in this second stage comprise ex-Co-Rh, Al-HTlc and ex-Co, Pd-La, Al-HTlc mixed oxides derived from hydrotalcite-like compounds and ion-exchanged Fe-ZSM-5 and Pd-ZSM-5 zeolites. Variables studied for the most promising deN_2O catalysts are the effect of the pretreatment, the sodium content of the ex-HTlc-catalysts, the presence of inhibitors in the feed stream, the addition of hydrocarbons to enhance the N_2O reduction in the second bed, and both time-on-stream and thermal stability of the catalytic system. Ex-Co-Rh, Al-HTlc proved to be the most active and stable catalyst, followed by Fe-ZSM-5, even when propene was added as reducing agent, which enhanced the conversion over the latter catalyst only. In an optimal configuration, at a temperature of 475 and 700 K in the first and second stage, respectively, molar conversions of 90 and 100% for NO_x and N_2O were achieved in a stable operation during 50 h. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: NO_x ; N_2O ; Dual-bed system; Pt/activated carbon; Calcined hydrotalcite; Ex-Co-Rh; Al-HTlc; Ex-Co; Pd-La; Al-HTlc; Fe-ZSM-5; Pd-ZSM-5; Propene

1. Introduction

The negative impact of anthropogenic NO_x emissions in our environment is well-established [1]. Thus, much effort has been put into the control of this pollutant from its respective sources. Coal-fired power plants and nitric acid factories are the main stationary

sources of NO_x emissions, while road traffic constitutes the most important mobile source (one-half of the NO_x man-made emissions) [2].

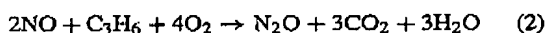
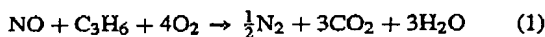
This decade, selective catalytic reduction of NO_x to N_2 under excess oxygen using hydrocarbons (HC-SCR) (reaction (1)), has been studied extensively, in order to establish a lean- deNO_x technology, applicable to diesel- and lean-burn gasoline-engine exhaust gas. A lot of new catalytic systems, including different noble and non-noble metals, different supports and different hydrocarbons have been

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investigated [3]. Cu-ZSM-5, a model zeolite-based catalyst for deNO_x reaction, presents a high selectivity towards N_2 for NO_x reduction avoiding the drawback of N_2O formation, but requires high operation temperatures ($>575\text{ K}$) and is deactivated by SO_2 and H_2O , showing poor hydrothermal properties [3]. Related catalysts are Co-beta and Fe-ZSM-5 [4,5]. Platinum-based catalysts on different supports have also shown an excellent catalytic behaviour, because of the low-temperature activity ($\sim 475\text{ K}$), thermal stability, and resistance to poisons [6–9]. An important drawback of this group of catalysts is the low N_2 selectivity, because N_2O is one of the major reaction products, reaction (2) [10,11].



Recently, Obuchi et al. [12] have performed a practical scale evaluation for selective reduction of NO_x with organic compounds under diesel exhaust gas conditions, identifying Pt-based $\text{Pt}/\text{Al}_2\text{O}_3$ and Pt-ZSM-5 as the most active in the low temperature range ($475\text{--}525\text{ K}$). They concluded, however, that the use of any single-phase catalyst does not satisfy the practical demand for car engines from both the activity (NO reduction) and selectivity (N_2O formation) aspects. This selectivity seems to be related with the metal used as active phase, and is independent of the support.

N_2O contributes to catalytic stratosphere ozone depletion and is a strong greenhouse effect gas [13,14]. N_2O is not only formed as a by-product from several processes, such as adipic acid production, nitric acid production, and circulating fluidised beds for combustion, but also as a consequence of measures to control the emission of other environmentally harmful species, like in the non-selective catalytic reduction (NSCR) of NO_x with cyanuric acid or urea and in aged three-way catalysts [15]. Therefore, with the increasing concerns about protecting our environment, there is a need to develop catalytic methods for the simultaneous control of both NO_x and N_2O emissions into the atmosphere.

Many catalytic systems have been reported as very active for N_2O decomposition, including supported metals, zeolites, and more recently, calcined hydrotalcite-like compounds, although most of the results published are not transferable to a real tail-gas

situation [15]. Recently, different authors have claimed the use of Fe-ZSM-5 for the effective reduction of N_2O with hydrocarbons in the presence of excess oxygen (5 vol% O_2) and water (10 vol% H_2O) [16], and even for the simultaneous reduction of N_2O and NO [17], which makes this catalyst a serious candidate for the removal of N_2O in the presence of inhibitors.

In a previous study [18], the use of activated carbon as support for Pt (Pt/AC) has been investigated for NO_x reduction with propene, under lean-burn conditions. A very active and stable catalytic system was developed, yielding NO_x conversions of 90% at a temperature of 475 K . For that system, the N_2 selectivity was approximately 30%, the formation of N_2O being a major problem. From this and other studies, it appears that the abatement of the formation of N_2O constitutes one of the major challenges for low-temperature lean- deNO_x systems. Pt/AC catalyst has shown similar activity, window temperature and N_2 selectivity than other Pt-based deNO_x catalysts, like Pt-ZSM-5 or Pt-USY. Furthermore, it has been proved to be superior to the $\text{Pt}/\text{Al}_2\text{O}_3$ [19].

In this paper, a practical alternative to reduce N_2O emissions operating with a low temperature and stable deNO_x catalyst based on Pt is presented, a dual-bed system, consisting of a deNO_x and deN_2O catalyst bed in series, for successive removal of both pollutants. In the first bed, the NO_x is reduced by propene over a Pt/AC catalyst; and in the second bed, the N_2O formed is decomposed catalytically into N_2 and O_2 over different mixed oxides derived from hydrotalcites and ion-exchanged metal zeolites. It is shown that this dual-bed system is robust and performs high conversions of both NO and N_2O without the use of a reductant. Under optimal conditions, the first bed operates at 475 K and the second bed at 700 K , achieving stable NO and N_2O conversion levels.

2. Experimental

2.1. Catalyst preparation

Table 1 lists the different samples prepared for this study. The preparation method and conditions are described below. These catalysts have been selected, based on their interesting behaviour in previous studies [15,18,20,21].

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Table 1
Data on catalysts of the present study

Catalyst	Metal loading (wt.%)	Atomic metal ratio ^a	S_A (m ² /g)
Pt/AC	1.0	—	950
Ex-Co-Rh, Al-HTlc ^b	—	2.5/0.05/1	144
Ex-Co, Pd-La, Al-HTlc ^b	—	2.5/0.5/0.8/1	79
Fe-ZSM-5 ^c	1.3	0.56/1	386
Pd-ZSM-5 ^c	1.0	0.23/1	386

^a The Al-content was taken as a reference for the other metal ions.

^b Na content in ex-Co-Rh, Al-HTlc was varied, ranging from 0.01 to 5.0 wt.%. In the other catalysts, it was <0.01 wt.%.

^c XRD patterns of the commercial and ion-exchanged zeolite match well with that of MFI (95% crystallinity). No impurity phase was observed.

2.1.1. Carbon-supported platinum (Pt/AC)

The carbon-supported platinum catalyst (Pt/AC) was prepared by the excess-solution impregnation method using ROX-0.8 (supplied by Norit) as catalyst support and H₂PtCl₆ as metal precursor [18]. Before the impregnation, the ROX-0.8 support was oxidised with HNO₃ (35 wt.%) at 375 K until dry. The product is referred to as ROXN. The details of this oxidation process are described elsewhere [22]. The impregnation process to obtain a 1 wt.% metal loading was carried out as follows: 10 ml of an aqueous solution of appropriate platinum concentration was added to 1 g activated carbon. After that, the activated carbon-solution mixture was first exposed to a N₂ flow for water evaporation, and then dried in an oven at 385 K, under vacuum, for a period of 12 h.

2.1.2. Mixed oxides derived from hydrotalcites (ex-Co-Rh, Al-HTlc and ex-Co, Pd-La, Al-HTlc)

Hydrotalcite-like materials [M_x²⁺M_{1-x}³⁺(OH)₂]^{z+}·[CO₃²⁻]_{x/2}·mH₂O were prepared by a standard aqueous co-precipitation method at constant pH and temperature [20]. These compounds were the precursors for the Co-Rh, Al and the Co, Pd-La, Al mixed oxides. A flow (2 l/h) of an aqueous solution of the metal nitrates in a desired molar ratio with a total cation (M²⁺ + M³⁺) concentration of 1.5 M was simultaneously mixed at room temperature under vigorous agitation with an alkaline solution of Na₂CO₃/NaOH, with the carbonate concentration in the molar ratio CO₃²⁻/Al³⁺ = 2. The pH of the mixtures was kept at 10, by adjusting the flow rate of the alkaline solution. Subsequently, the slurry was aged at 340 K for 18 h under mild stirring. Finally, the material was cooled to room temperature, filtered, washed with

large amounts of warm (305 K) deionised water, and dried at 365 K for 12 h. Ex-Co-Rh, Al-HTlc was prepared with different sodium contents (0.01–5.0 wt.% Na). This was achieved by adding a suitable amount of sodium carbonate to the washed coprecipitate. The hydrotalcites were calcined for 18 h in static air raising the temperature to 725 K at a rate of 10 K/min. These samples are indicated by ex-HTlcs.

2.1.3. Metal-exchanged zeolites (Fe-ZSM-5 and Pd-ZSM-5)

Iron(III)- and palladium(II)-exchanged ZSM-5 zeolites have been prepared by a conventional ion-exchange method. The parent ammonium form of ZSM-5 (SiO₂/Al₂O₃ = 75) was provided by P&Q Corporation (BET: 386 m²/g). The exchange was carried out under vigorous stirring, using diluted aqueous solution (0.30 mM) of iron nitrate, Fe(NO₃)₃·9H₂O, or palladium nitrate, Pd(NO₃)₂, in a solid-to-liquid ratio of 1 g/l at 295 K, during 15 h. The zeolites were then filtered and washed thoroughly with deionised water at room temperature before drying at 385 K overnight. Finally, the dry zeolites were subjected to calcination in air at 825 K for 5 h.

2.2. Catalyst characterisation

The characterisation of Pt/AC, the hydrotalcites and the mixed oxides used in this study has been described extensively in former articles [18,21,22].

Zeolite-based catalysts have been characterised by X-ray diffraction (XRD) and inductive coupled plasma-optical emission spectroscopy (ICP-OES) and atomic absorption spectroscopy (AAS). XRD patterns of the zeolite before and after exchange was

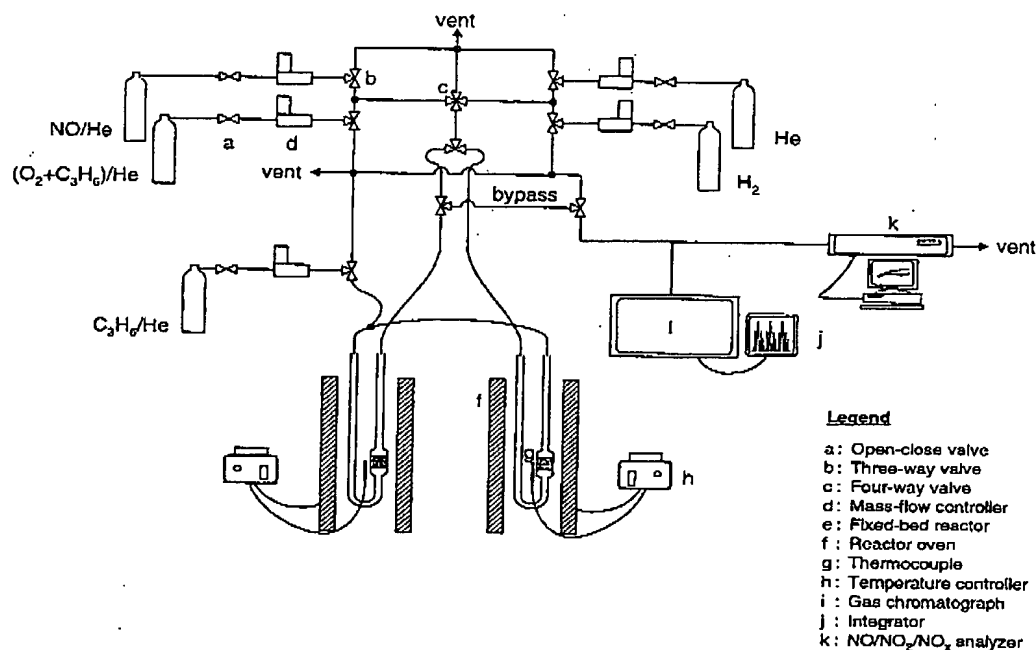


Fig. 1. Detailed scheme of the experimental set-up to carry out the catalytic tests.

obtained with a Philips PW 1830/40 diffractometer using a graphite monochromator and $\text{CuK}\alpha$ radiation. Data were collected in the 2θ range of $5\text{--}50^\circ$ at a scan rate of $0.5^\circ/\text{min}$. The metal content of the zeolites was determined by ICP-OES (Perkin-Elmer Plasma 40 (Si) and Optima 3000DV (axial)) and AAS (Perkin-Elmer 1100). Table 1 summarises the most relevant characterisation results.

2.3. Experimental system

2.3.1. Set-up

Catalytic activity measurements were carried out in two quartz-tube fixed-bed reactors in series. The product gases were continuously analyzed with a chemiluminescence $\text{NO}\text{--}\text{NO}_2\text{--}\text{NO}_x$ analyzer (Thermo Environmental, Model 42H), and discontinuously analyzed for the other gases by a gas chromatograph. The chromatograph (HP 5890 Series II) is equipped with a thermal conductivity detector, using two serial

columns (Porapak Q 80/100, for separation of CO_2 , N_2O , H_2O and C_3H_6 , and Molecular Sieve 13X, for O_2 , N_2 , and CO) joined by a six-way valve. A scheme of the experimental system is shown in Fig. 1. Both beds operate in plug flow and in isothermal conditions with independent temperature control. Application of the criteria to check the presence of mass and heat transport limitations in the reactor revealed that these restraints were absent [23]. The reactor characteristics and the operating conditions are shown in Table 2.

2.3.2. System development

The reactor configurations used in this study are summarised in Fig. 2. Different types of experiments were undertaken. Firstly, the behaviour of each bed was studied individually for the specific reaction (NO_x reduction or N_2O decomposition) at the relevant conditions (configurations a and b). Secondly, a combined dual-bed catalytic reactor was designed in which NO_x and N_2O were successively eliminated (configuration

Table 2
Description of the reactor system and the operating conditions during the activity and stability tests

Parameter	Bed 1 (deNO _x)	Bed 2 (deN ₂ O)
Reactor diameter (mm)	15	15
Reactor bed length (mm)	35	35
Total flow (ml/min STP)	60	60
Total pressure (bar)	1	1
Space velocity ^a (ml/g·h)	14 400	14 400
Space time ^b (g min/mol)	100	300
Catalyst mass (g)	0.25	0.25
Catalyst shape	extrudates	particles
Catalyst dimensions (mm)	0.5 × 2.0	0.1–0.2
Catalyst pretreatments	100% H ₂ , 12 h, 625 K	He, 1 h, 700 K 5% O ₂ in He, 1 h, 700 K 20% H ₂ in He, 1/2 h, 700 K
Temperature range (K)	300–775	375–975

^a Defined as F_T/W , F_T being the total volumetric flow and W the catalyst mass.

^b Defined as W/F_{NO}^0 or $W/F_{N_2O}^0$, W being the catalyst mass and F_i^0 the inlet molar flow of component i .

c). Finally, the system was extended by secondary hydrocarbon injection at the inlet of the second bed (configuration d).

2.3.3. Procedures

After the pretreatment, which is specified in Table 2, the temperature was decreased to the desired value

independently in each bed and the feed mixture was passed over the system.

The feed to the dual-bed system consists of a gas mixture containing (A) 1000 ppm NO and 5 vol% O₂ and (B) 1000 ppm C₃H₆, balanced in He. When the second bed was tested individually, the feed consists of (C) 300 ppm N₂O in He. A stream containing (D) 400 ppm C₃H₆ in He was used for the hydrocarbon addition in the second bed.

Three different operation modes have been applied to study both the individual and the combined systems: (i) temperature programmed reactions, in transient operation, at 3 K/min up to 775 K (bed 1) and 975 K (bed 2), (ii) activity tests in steady state conditions in the same temperature range as used in (i), and (iii) stability tests under isothermal operation (475 K for bed 1, and between 700 and 975 K for bed 2). Generally, 1 hr after a change of conditions the NO_x and N₂O conversion levels were constant and the steady state was considered to be reached.

3. Results and discussion

3.1. deNO_x process

The deNO_x reaction over the Pt/AC catalyst has been recently studied by the authors [18]. Fig. 3 shows the evolution of the nitrogen products as a function of temperature as obtained by temperature programmed

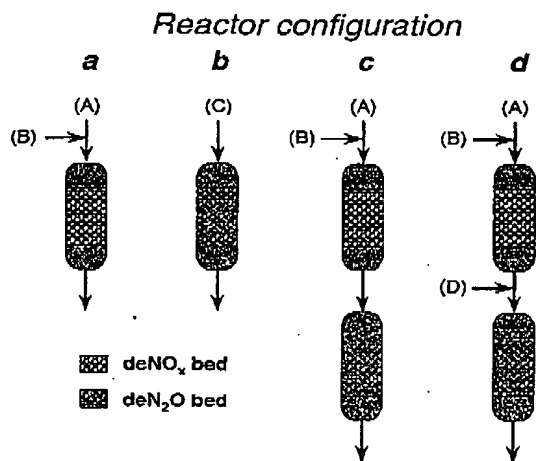


Fig. 2. Different reactor configurations adopted in the present: (a) deNO_x bed, (b) deN₂O bed, (c) combined system, (d) system with addition of hydrocarbon to the deN₂O bed, (A) = 1000 ppm NO + 5 vol% O₂, (B) = 1000 ppm C₃H₆, (C) = 300 ppm N₂O, (D) = 400 ppm C₃H₆. Balance gas in all the streams: He.

experiments. The purpose of this technique is the determination of the optimal temperature for the deNO_x process, in order to maximise the NO reduction, being 475 K. In general, two stages in the NO concentration curves of the Pt/AC catalyst can be distinguished. In the adsorption stage, at temperatures below 325 K, in which the sample completely adsorbs the reactants (NO_x and C_3H_6) as a consequence of the characteristic high surface area of the activated carbons used (BET surface area: $950 \text{ m}^2/\text{g}$ for ROXN). In the second stage, at temperatures above 325 K, desorption and reaction processes take place simultaneously. The desorption of the previously adsorbed compounds from the support in this temperature range provokes the observation of a higher reactant concentration at the outlet than at the inlet of the catalytic bed. In the reaction stage, NO reduction and C_3H_6 combustion are the dominant processes. Formation of N_2O and N_2 already starts at temperatures of 325 K. The N_2O profile reaches a maximum when the NO conversion reaches the optimal value, as typically observed for Pt-based catalysts in deNO_x reaction [10].

In the isothermal experiments with Pt/AC at the selected temperature of 475 K, the catalyst has shown a high activity (molar conversion of 90%), as well as a stable activity during time-on-stream tests for 100 h. However, the low operating temperature of the Pt/AC catalyst results in the formation of large amounts of nitrous oxide. From 1000 ppm of NO_x in the feed stream, 300 ppm of N_2O are formed as a by-product, leading to a N_2 -selectivity of 30% (Fig. 3). This

selectivity is defined as:

$$\text{Selectivity } \text{N}_2 = \frac{\% \text{N}_2 \text{ outlet}}{(\% \text{N}_2 + \% \text{N}_2\text{O}) \text{ outlet}} \quad (3)$$

The maximum formation of nitrous oxide corresponds with the minimum value of NO concentration, in good agreement with the results reported in literature for Pt-based catalysts [10–12]. At higher temperatures, where the N_2 selectivity of the reaction increases, due to the reasons mentioned above, the conversion of the NO_x is lower, due to the higher efficiency of the propene combustion reaction.

Several mechanisms have been proposed to explain the HC-SCR reaction pathways on Pt-based catalysts [3]. In general, the most accepted is that formulated by Burch et al., based on the results of the SCR by propene on 1 wt.% Pt/ Al_2O_3 , using the temporal analysis of products technique (TAP) [24]. A two-step mechanism is initiated by one molecule of hydrocarbon reducing a small region of surface Pt–O into metallic Pt (oxygen 'clean-off'). On these vacant, reduced sites, the adsorption/dissociation of NO proceeds, being temperature dependent. At lower temperatures, NO adsorbs mainly molecularly, and only a fraction is dissociated. The adsorbed NO is then able to recombine with an N-atom, which explains the formation of N_2O . At high temperature NO dissociation takes place and, as a consequence, N_2 rather than N_2O is formed. Further the high concentration of oxygen (lean conditions) limits the availability of reduced sites by reoxidation and thus, limiting the NO-dissociation process.

3.2. Combined deNO_x - deN_2O process

In order to improve the process in terms of selectivity, a combined system of two catalytic beds in series has been developed. The second bed being a successive stage where the N_2O from the first bed is catalytically decomposed into N_2 and O_2 (Fig. 2c). This alternative could be considered, to some extent, as a kind of a macroscopic bifunctional solution. The catalyst placed in the second bed should be able to decompose the N_2O with no deactivation or inhibition by the additional gases in the incoming feed stream, maintaining a high activity at relatively low temperatures, exhibiting a constant time-on-stream activity as well as

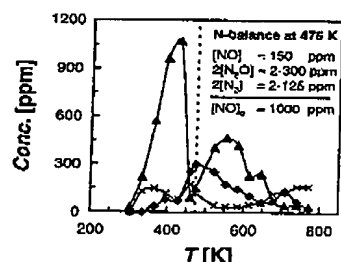


Fig. 3. Concentration profiles for (Δ) NO, (\blacklozenge) N_2O , and (\times) N_2 as obtained by temperature programmed reaction experiment for the Pt/AC catalyst. Feed: 1000 ppm NO_x , 1000 ppm C_3H_6 , 5 vol% O_2 , balance He; flow rate = 60 ml/min; catalyst = 0.25 g; heating rate = 3 K/min. Dashed line indicates the temperature in isothermal operation.

thermal stability. In order to accomplish this requirement, different promising catalytic systems for the removal of N_2O have been considered. The first group consists of calcined hydrotalcites based on Co-Rh and Co, Pd-La, which have been described as very active catalysts for the N_2O decomposition [20,21]. The second group is formed by ion-exchanged metal zeolites of Pd or Fe. Pd-ZSM-5 has also shown a promising performance in the reaction [25], and Fe-ZSM-5, which is less active for the N_2O decomposition under 'dry' conditions, presents an uncommon behaviour in the presence of other components, preserving and even improving its activity in situations where other catalysts would be severely affected [26]. In addition, Fe-ZSM-5 has been successfully employed for simultaneous removal of NO and N_2O using hydrocarbons as reductant [17].

The gas composition of the product stream from the first bed was determined in the stability test at 475 K to be: 150 ppm NO, 300 ppm N_2O , 125 ppm N_2 , 4.6 vol% O_2 , 0.3 vol% CO_2 , and 0.3 vol% H_2O , balance He. The water value was calculated from the combustion of propene, which was completely converted to CO_2 and H_2O . Fig. 4 displays the conversion results achieved for the catalysts of the second bed in the combined system. All the samples were pretreated in helium under the conditions mentioned in Table 2. Ex-Co-Rh,Al-HTlc with a Na content of 0.75 wt.% proved to be the most active system, reaching N_2O conversions of 100% at around 700 K. Fe-ZSM-5 also presents a high activity, although far lower than the ex-hydrotalcite. Both Pd-based catalysts,

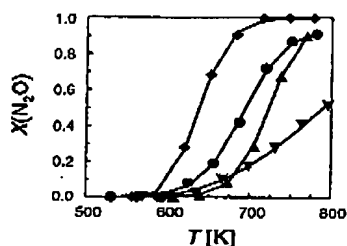


Fig. 4. Conversion of N_2O as a function of temperature in the second bed for the combined system for (◆) ex-Co-Rh, Al-HTlc, (●) Fe-ZSM-5, (▲) ex-Co, Pd-La, Al-HTlc, and (▼) Pd-ZSM-5. Feed: 150 ppm NO, 300 ppm N_2O , 125 ppm N_2 , 4.6 vol% O_2 , 0.3 vol% CO_2 , 0.3 vol% H_2O , balance He; flow rate = 60 ml/min; catalyst = 0.25 g.

ex-Co, Pd-La, Al-HTlc and Pd-ZSM-5, present poor activities compared to the above-mentioned catalysts, with Pd-ZSM-5 being the least active. For the most active catalysts of each group, i.e. ex-Co-Rh, Al-HTlc and Fe-ZSM-5, the stability during time-on-stream was checked for a period of 50 h at 700 and 750 K, respectively. Both have maintained the initial conversion (see Fig. 10).

3.3. Effect of inhibitors in the feed stream

Other gases in the mixture that contain N_2O can affect its destruction rate by competitive adsorption, by deactivation due to irreversible blocking (poisoning), or by alternative reactions. Important in this respect are O_2 , H_2O , NO_x , and SO_2 . Their effects are primarily important for practical applications, but are far less studied than the 'pure' reaction [15]. Activity tests were carried out with a feed containing the same amount of N_2O formed after the first bed, i.e. 300 ppm, using helium as balance gas, and the same total flow, space velocity, and pressure, as defined in Table 2. The conversion curves of N_2O versus temperature for the different catalytic systems are shown in Fig. 5. In general, the activity of the catalysts is significantly depressed by the presence of additional

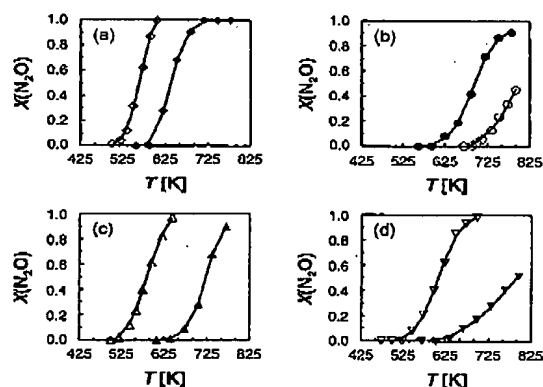


Fig. 5. Effect of the other components on the de N_2O catalysts: (a) ex-Co-Rh,Al-HTlc, (b) Fe-ZSM-5, (c) ex-Co, Pd-La, Al-HTlc, and (d) Pd-ZSM-5. Open symbols: feed 300 ppm N_2O , balance He; flow rate = 60 ml/min; catalyst = 0.25 g. Solid symbols: conditions as described in the legend of Fig. 4.

gases. Especially, those containing Pd were most affected. Fe-ZSM-5 presents a deviating behaviour: its activity increased when additional gases were present.

Swamy et al. [27] have reported no oxygen inhibition over ex-Co-Rh,Al-HTlc (Co/Al = 2/1 and 0.7 wt.% Rh) at relatively high temperature (725 K). Pd-ZSM-5 and Fe-ZSM-5 have hardly shown any inhibition by O₂ [15,26,28,29]. CO₂ has not been reported as a poison for the N₂O decomposition reaction, unless it leads to stable carbonate formation under relevant conditions [30]. On the other hand, the remaining NO from the first bed (150 ppm) and the water vapor from the hydrocarbon combustion reaction (0.3 vol%) can act as serious inhibitors. H₂O concentrations of 0.5 vol% have been reported to lower dramatically the N₂O decomposition [31]. NO has been identified as a strong inhibitor for the N₂O decomposition catalysts, through formation of surface nitrites and nitrates. Nitrite complex formation (M–NO₂ or M–ONO) is favored in zeolites, while the more stable nitrate complex formation (M–NO₃ or M–ONO₂) is generally observed in oxides [32]. For Pd-ZSM-5, this inhibition has been identified at 700 K [33], but for Fe-ZSM-5 a positive effect has been reported [26,34]. The presence of reducing agents, e.g. in the latter case NO and SO₂, may enhance tremendously the surface oxygen removal, reaction (4), thereby accelerating the N₂O destruction.



This indicates that the oxygen removal is the difficult step in the reaction. In fact, in the steady state, the active sites in Fe-ZSM-5 are nearly fully oxidised. Kinetically, the blocking of sites of the observed NO adsorption on the Fe catalyst is negligible compared to the enhancement achieved by the oxygen removal effect [26]. In the same study, H₂O was considered as strong inhibitor for Fe-ZSM-5, but in our dual-bed system, where both H₂O and NO are present, this effect is not detected. Therefore, with the exception of the Fe-ZSM-5, it can be concluded that both the unconverted NO and the H₂O formed in the combustion of propene from the first stage are mainly responsible for the general decline of the N₂O conversion over the catalysts in this study.

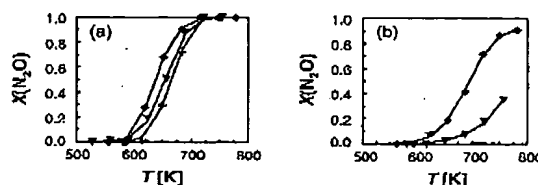


Fig. 6. Effect of the pretreatment on the catalytic activity for (a) ex-Co-Rh,Al-HTlc, and (b) Fe-ZSM-5, with (♦) He, 1 h, 700 K, (▼) 5 vol% O₂ in He, 1 h, 700 K, and (+) 20 vol% H₂ in He, 1/2 h, 700 K. Feed: conditions as described in the legend of Fig. 4.

3.4. Effect of pretreatment

The effect of catalyst pretreatment has been studied for the ex-Co-Rh,Al-HTlc and the Fe-ZSM-5. The sensitivity of the catalysts towards oxidative (O₂ in He), reductive (H₂ in He), and inert (He) treatment were investigated. As shown in Fig. 6a, a pretreatment in an inert gas produces an optimal behaviour in the ex-Co-Rh,Al-HTlc, followed by the pretreatment in oxygen and in hydrogen, although no large differences were found. This result was expected due to the composition of the reacting gas. Its oxygen content (4.6 vol%) will reconstruct the pretreated surface in a short time, and in the end, the catalyst surface is oxidised, showing no dependence on pretreatment.

Oxidative pretreatment in Fe-ZSM-5 leads to a significantly less active catalyst than pretreatment in He (Fig. 6b). The pretreatment in O₂ will produce the formation of Fe³⁺. Fe-ZSM-5 seems to operate in an oxidation–reduction cycle Fe²⁺/Fe³⁺ [34]. The decomposition mechanism indicates that after N₂O interaction with the catalyst surface, Fe³⁺–O[–] is formed, rapidly followed by a migration of the deposited oxygen to lattice oxygen and reduction back to Fe²⁺. Therefore, if the oxidative pretreatment tends to stabilise Fe³⁺ species, the activity will be somehow depressed, because the active initial oxidation state of the catalyst's active site in the catalytic cycle is absent.

3.5. Effect of the sodium content

Ex-Co-Rh,Al-HTlc has been prepared with different sodium contents, ranging from 0.01 to 5.0 wt.% Na. This procedure has been described as more effective to promote the N₂O decomposition reaction than

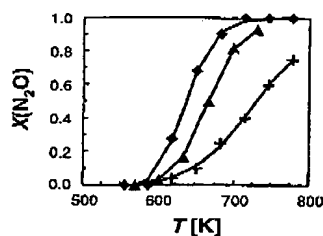


Fig. 7. Effect of the sodium content in the catalytic activity for the ex-Co-Rh,Al-HTlc: (Δ) 5 wt.% Na, (\blacklozenge) 0.75 wt.% Na, (+) 0.01 wt.% Na. Pretreatment: He, 1 h, 700 K. Feed: conditions as described in the legend of Fig. 4.

when Na is naturally present (from the co-precipitation step) [27]. Fig. 7 shows the conversion–temperature curves for the ex-Co-Rh,Al-HTlc at different Na wt.% levels. Apparently, there is an optimal loading in the catalyst (0.75 wt.%), which leads to the highest conversion. The catalyst with the lowest Na content (0.01 wt.%) has the poorest activity, while a higher loading (5 wt.%) also provokes a dramatic decrease of activity with respect to the optimum. Swamy et al. [27] have reported the positive effect of Na addition to ex-Co-Al-HTlc, as well as other alkaline metals (K, Li) and Mg, in the stability of the catalyst for the decomposition of N_2O . In their case the optimal loading of Na was between 1 and 2 wt.%. It might be feasible that Na modifies the electronic properties of the active phase, enabling an easier electron transfer from or to the catalyst surface and/or stabilises the Co(II) oxidation state. Further research should be carried out in order to clarify this remarkable observation.

3.6. Effect of the HC addition

The addition of propene to feed to the second bed (Fig. 2d) was done in order to evaluate the performance of the two most active catalysts in the reduction of N_2O , since catalytic reduction of N_2O with hydrocarbons can result in a very active and stable system in the presence of inhibitors, like O_2 and H_2O [16], and even in simultaneous NO and N_2O reduction, as in the case of Fe-ZSM-5 [17].

The results achieved for these catalysts are shown in Fig. 8. For the ex-Co-Rh,Al-HTlc pretreated in inert conditions the addition of 400 ppm of propene in He has no positive effect for the N_2O removal

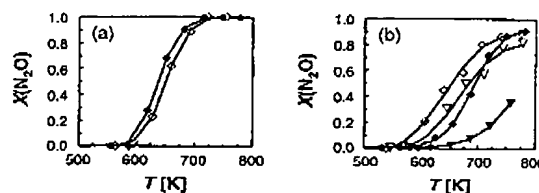


Fig. 8. Effect of the secondary hydrocarbon injection on the N_2O conversion for (a) ex-Co-Rh,Al-HTlc and (b) Fe-ZSM-5. Open symbols: after addition of 400 ppm C_3H_6 in He to feed stream as described in the legend of Fig. 4 (solid symbols). Catalyst pretreatment: ($\blacklozenge, \blacktriangledown$): He, 1 h, 700 K, ($\blacktriangledown, \blacktriangledown$) 5 vol.% O_2 in He, 1 h, 700 K.

activity, even a slight deactivation can be observed with respect to the system operating without hydrocarbon (Fig. 8a). The same behaviour has been observed in the H_2 - and O_2 -pretreated catalysts (not shown). These phenomena can be easily explained by analysis of the different gases involved in temperature programmed reaction experiments (Fig. 9a). For ex-Co-Rh,Al-HTlc, the N_2O decomposition reaction starts at around 600 K, while C_3H_6 conversion to CO_2 was already completed at 500 K. Therefore, almost no reducing agent is present in the catalyst bed at temperatures where N_2O decomposition starts to occur. Propene combustion and N_2O conversion seem to be rather independent from each other on this catalyst. On the other hand, Co-exchanged ZSM-5 was shown to be active for the simultaneous removal of N_2O and NO by methane [35]. To understand this disparity, one has to regard the presence of Co_3O_4 -spinel within the Co-HTlc. Bulk Co_3O_4 is well-known as combustion catalyst [36]. In slightly over-exchanged Co-beta the presence of a very small amount of Co_3O_4 enhances the HC-SCR-activity at low temperature due to oxidative hydrocarbon activation, which can be considered as cooperative effect (Co-Beta 4 wt.% Co) [37]. In our case, the absolute amount of Co_3O_4 is obviously much higher, explaining the occurrence of the non-selective combustion of propene.

Fe-ZSM-5 showed an enhancement of the N_2O conversion after injection of hydrocarbon. This is qualitatively true for the He- as well as for the O_2 -pretreated catalyst, although the enhancement was more pronounced in the case of the O_2 -pretreated catalyst. In contrast with the Co-catalyst, combustion of the propene and N_2O conversion occurs in the same tem-

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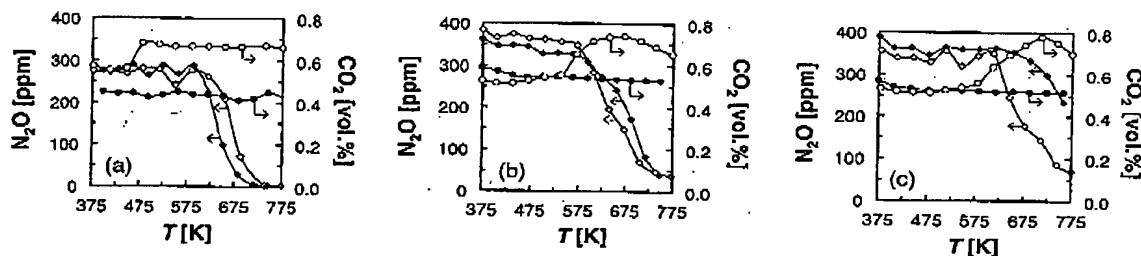
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Fig. 9. Exit concentration profiles for (◆,◇) N_2O and (●,○) CO_2 obtained in the temperature programmed reaction experiment for (a) ex-Co-Rh,Al-HTlc (He), (b) Fe-ZSM-5 (He), and (c) Fe-ZSM-5 (O_2). Open symbols with addition of 400 ppm C_3H_6 in He to feed stream as described in the legend of Fig. 4, solid symbols without hydrocarbon addition. The pretreatment is expressed between brackets after the catalyst formulation.

perature range over this catalyst, which can be seen from Fig. 9b and c. Another difference worthwhile to note, is the fact that obviously considerable amounts of hydrocarbon adsorb on the catalyst surface at lower temperatures. This is indicated by the CO_2 formation curve exceeding the stoichiometric level of 0.42 vol.% that is theoretically generated by total combustion of propene. The reason for that behaviour is the transient regime of the TPR experiment, as explained in Section 2.3. The specific capabilities of neutral and acidic zeolites for hydrocarbon adsorption are well established. Furthermore, the formation of 'carbonaceous species' (hydrocarbon intermediates with a relatively long life-time) is well documented due to research on HC-SCR on metal exchanged zeolites [3].

Kögel et al. [17] studied Fe-ZSM-5, prepared by solid-state ion-exchange, for the simultaneous removal of NO and N_2O by propene (among other hydrocarbons) under steady state conditions. At 725 K they observed a NO conversion of 15%. At the same temperature, we also observed a decrease of the NO level, corresponding to a conversion of ~10%.

3.7. Thermostability

The reactions involved in N_2O destruction are all exothermic, so the thermostability of the catalysts should be taken into account in most cases, also in relation to the presence of H_2O . This aspect seems mainly important for the high concentration levels in adipic acid plants [15], where levels of 30–50% of N_2O lead to adiabatic temperature rises of 500–700 K.

but it is also important because of overheating phenomena inside de NO_x converters in cars [38].

The thermal stability of the most promising catalysts (ex-Co-Rh,Al-HTlc and Fe-ZSM-5) was studied by carrying out experiments at high temperatures in the combined system of two beds. The operation comprises the raise of temperature of the second bed from 700–775 K (optimal operation temperature) up to 975 K at intervals of 100 K (10 K/min), and keeping these conditions for 10 h (in isothermal mode). The decrease of the temperature from the maximum value reached (975 K) to lower temperatures did not produce any deactivation of both samples.

Fe-ZSM-5 has demonstrated a stable operation over the whole range of temperatures, which is in a good agreement with the intrinsic features of these materials. In the same way, ex-Co-Rh,Al-HTlc exhibited a stable behaviour at the process conditions. Apparently, the raise in the reaction temperature above that of the preparation did not have any negative influence [39], neither on the activity nor on the stability, which were maintained at the original level. The catalyst is composed of stable spinel structures, resistant to sintering under the applied conditions.

3.8. Optimal configurations and evaluation

Based on the previous results, Fig. 10 shows schematically the dual-bed configuration proposed with the process values for the most favourable conditions with ex-Co-Rh,Al-HTlc and Fe-ZSM-5 as N_2O decomposing catalysts. For the latter case the system has to be equipped with an additional hydrocarbon

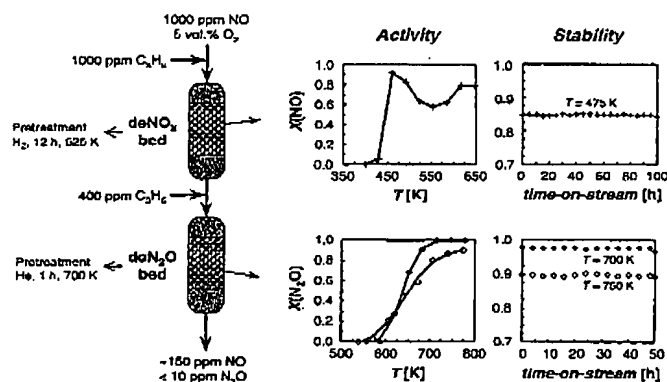


Fig. 10. Activity and stability of the catalysts in the dual-bed deNO_x-deN₂O system. (+) Pt/AC, (◆) ex-Co-Rh,Al-HTlc, and (◇) Fe-ZSM-5 (with injection of 400 ppm C₃H₈ in He). Feed: conditions as described in the legend of Fig. 4. The activity and stability of the second bed were recorded for a temperature in the first bed of 475 K.

injection to achieve sufficiently high conversion levels. Both reactors operate at these temperatures at similar space velocities, so will have similar bed volumes.

Kögel et al. [17] reported the simultaneous removal of NO and N₂O over the single catalyst Fe-ZSM-5. Although this bifunctionality is, in theory, very attractive for application in a process generating both gases, the catalyst does not exhibit a sufficient activity. At the maximum NO removal (40% at 575 K), N₂O conversion was 5%, using propane as reductant, and when the N₂O decomposition is favoured to achieve complete removal (at 775 K), NO conversion was 15%. This result is in a good agreement with our observation of a temperature window for Fe-ZSM-5 for a total N₂O removal with only low NO conversion in the second bed. In addition, especially in the low temperature range, important amounts of unconverted hydrocarbon as well as carbon monoxide were formed in side reactions in their study.

In view of the features of the Fe-ZSM-5 system to accomplish a single-stage NO-N₂O reduction and those of the dual-bed system demonstrates the advantages of operation with a dual-bed reactor, which allows high conversions of both species. In addition, the reducing agent used (in both stages of the system) was completely converted to CO₂, eliminating a further treatment of the exhaust gas.

It is noted that practical application of the dual-bed system is still unfeasible based on the extrapolation of our results from laboratory-scale conditions to a realistic car exhaust situation. For that application, the required activity of catalyst has to be increased by about a factor of 10, taking into account typical space velocities (SV = 100 000 versus 14 400 h⁻¹) and flow rates of exhausts in cars (20–150 Nm³/h versus 60 ml/min). Recent work by Long et al. [11] for deNO_x HC-SCR with 1.0 wt.% Pt/MCM-41 indicates that sufficiently high activities may come into reach. This catalyst presents high activities for NO reduction, achieving a maximum conversion of 80% at a temperature of 500 K and a space velocity of 75 000 h⁻¹ with complete hydrocarbon combustion to CO₂ (besides H₂O). The oxygen concentration used, however, was relatively low (2.0 vol%), and a strong oxygen dependency generally exists going to higher concentrations (5.0 vol%).

Apart from this catalyst optimisation aspect, current catalysts are not yet suited for a single-stage operation in lean-burn NO_x removal, and a dual-bed operation, with optimal catalyst choice for the specific reaction and the independent operation temperature in each bed, is for the moment the preferred option. The application of the dual-bed system is not restricted to car exhausts, because several flue gases, such as of

nitric acid plants and fluidised bed combustors contain significant amounts of NO and N₂O. In these cases the stationary process conditions allow more flexibility than mobile sources for optimisation of the exhaust gas treatment.

4. Conclusions

A dual-bed catalytic system for removal of NO and N₂O in lean deNO_x HC-SCR proved to operate with a high and stable activity. A first bed, containing a Pt/AC catalyst, leads to a high NO molar conversion (90%) at low temperature (475 K), producing large amount of N₂O (300 ppm), which is catalytically decomposed (100% conversion) in a second bed at optimal temperatures between 700 and 775 K. An ex-Co-Rh,Al-HTlc catalyst, with 0.75 wt.% Na, produces the best result in this stage, followed by Fe-ZSM-5. The activity of Pd-based catalysts (both mixed oxide and zeolite-based) was considerably suppressed due to the inhibitors coming with the N₂O, especially NO and H₂O. The activity of ex-Co-Rh,Al-HTlc is also affected under realistic conditions. In contrast, Fe-ZSM-5 presents an improved activity in the process stream, attributed to the presence of the remaining NO from the first bed, acting as a reducing agent. The influence of the oxidative pretreatment in the catalytic activity was more pronounced in the zeolite-based catalyst (Fe-ZSM-5), than in the calcined hydrotalcite (ex-Co-Rh,Al-HTlc), a pretreatment in He being the optimal for both catalysts. The addition of hydrocarbons in the second bed produced a slight deactivation in the activity of the mixed oxide, whereas the behaviour of the Fe-ZSM-5 was substantially improved. In any case, the ex-Co-Rh,Al-HTlc catalyst shows its superiority, being better for the fuel economy, because N₂O decomposition does not require reducing agents.

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